

Upper critical field of aligned $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ superconductor by magnetization measurement

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We present magnetization measurements for the upper critical field H_{c2} on aligned $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ superconductors with magnetic field parallel to CoO_2 layers. The temperature-dependent part of the normal-state magnetization $M(H, T)$ can be well scaled with Brillouin function, suggesting the existence of impurity moments. By subtracting the contribution of the magnetic impurity moments, a well defined onset of superconducting diamagnetism allows the in-field superconducting transition temperature $T_c(H)$ accurately determined. No superconducting transition was observed down to 1.9 K under an applied field of 8 Tesla. The result suggests that the $H_{c2}^{\parallel ab}(0)$ value is just within the Pauli paramagnetic limit, supporting spin-singlet superconductivity in the cobalt oxyhydrate superconductor. Additionally, the upward curvature near T_c in the $H_{c2}^{\parallel ab} - T$ phase diagram was confirmed to be intrinsic. Possible origin of the anomaly was discussed.

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I. INTRODUCTION

Superconductivity in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ ¹ has attracted much attention in recent years. The new layered superconductor exhibits both similarities and differences with the well-known cuprate superconductors, shedding light on the challenging issue of understanding high- T_c superconductivity.² At present, evidences of unconventional superconductivity in this material have been indicated or implied by experimental researches^{3,4,5,6,7,8,9} as well as by theoretical studies.^{10,11,12} However, some of the basic questions on the superconductivity remain open. For example, an unprecedented number of proposals have been suggested for the superconducting pairing symmetry.¹³ Obviously, clarification of the spin state of Cooper pairs is crucial to this problem.

Upper critical field H_{c2} is among the most important superconducting parameters since it not only directly correlates with the superconducting coherence length ξ , the size of Cooper pairs, but gives a clue to the pairing symmetry. However, the determination of $H_{c2}(0)$ in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ superconductor remains controversial. Resistivity,¹⁴ heat capacity^{9,15} and ⁵⁹Co-NMR¹⁶ measurements suggested that the $H_{c2}(0)$ value was within the Pauli paramagnetic limit^{17,18} $H_P \approx 8.3$ T, implying spin-singlet state for the Cooper pairs. In contrast, a much larger $H_{c2}(0)$ value, far exceeding the Pauli paramagnetic limit, was inferred from magnetization measurements,^{4,8} which favors spin-triplet superconductivity. Another issue is the observation of an abrupt slope change of H_{c2} (or upward curvature) on the $H_{c2} - T$ curve near T_c ,^{8,9} which was explained in terms of field-induced pairing symmetry transition.^{8,19} Since the anomalous curvature was ob-

served on randomly oriented polycrystalline sample, the anomaly could be an extrinsic phenomenon due to the anisotropy of H_{c2} .⁹

In order to clarify these issues we carried out magnetization measurements for H_{c2} on *aligned* cobalt oxyhydrate superconductors. In principle, $H_{c2} - T$ phase diagram can be obtained by determining the superconducting transition temperature under different magnetic field, *i.e.*, $T_c(H)$. In the case of the cobalt oxyhydrate superconductor, however, determination of $T_c(H)$ becomes difficult especially at high field due to the susceptibility upturn in the normal state.⁴ We found that the temperature-dependent part of normal-state magnetization can be well scaled in terms of Brillouin function, suggesting that the susceptibility upturn above T_c arises from impurity moments rather than spin fluctuation. The in-field superconducting transition temperature $T_c(H)$ was then accurately determined by subtracting the contribution of magnetic impurity. Consequently the estimated $H_{c2}(0)$ was found to be just within the Pauli paramagnetic limit. Besides, the upward curvature near T_c in the $H_{c2} - T$ phase diagram was confirmed to be intrinsic.

II. EXPERIMENT

Polycrystalline samples of the cobalt oxyhydrate superconductor were synthesized through three steps as described previously.^{5,20} First, parent compound $\text{Na}_{0.7}\text{CoO}_2$ was prepared by a solid-state reaction from high purity Na_2CO_3 and Co_3O_4 powders. Second, the sodium was adequately deintercalated by employing $\text{Br}_2/\text{CH}_3\text{CN}$ as an oxidizing agent. Third, the resulted Na_xCoO_2 samples with $x \sim 0.33$ were then hydrated at room temperature in saturated NaCl solution for 10 days. X-ray diffraction confirmed that the obtained sam-

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ples were single phase. The chemical composition of the sample was determined by the techniques described previously.²⁰ The sample used in present study has the chemical composition of $\text{Na}_{0.33}(\text{H}_3\text{O})_{0.02}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$.

We made use of the large anisotropy in magnetization²¹ to align the powder samples. Since the easy magnetization direction is along the *ab* planes, the crystalline grains can be aligned with the *ab* planes parallel to the external field in a liquid medium by applying a high magnetic field. Upon cooling down under the field the medium freezes, thus the grain orientation is fixed. In our experiment we chose the saturated NaCl solution as the medium in order to suppress the ion exchange between hydroniums and Na^+ ions.^{20,22,23} Mixture of the powdered superconductor and saturated NaCl solution in a teflon container was frozen below 250 K under an 8 T field. Magnetization measurement, performed on a Quantum Design PPMS facility, showed that the aligned sample had relatively large magnetization compared with the non-aligned sample.

III. RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of ac magnetic susceptibility for $\text{Na}_{0.33}(\text{H}_3\text{O})_{0.02}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ sample with the field parallel to *ab* planes. Sharp superconducting transition can be seen at 4.5 K. The diamagnetic signal at 2 K is among the best results (for polycrystalline samples) in the literatures,^{1,9,15} suggesting high quality of the present sample. The inset shows an expanded plot for the normal-state susceptibility. One can see an obvious susceptibility upturn with decreasing temperature. Similar phenomenon was previously reported.^{4,8}

There exists at least two kinds of explanations about the susceptibility upturn behavior. One possibility is that the susceptibility enhancement above T_c is relevant to spin fluctuations.^{4,24,25} However, the enhancement was sample dependent.²⁶ Another explanation simply concerns the paramagnetic impurity.^{4,21} The applied field lines up the impurity moments hence induces a magnetization, which can be expressed by the following equation,

$$M = ng_J\mu_B JB_J(\alpha), \quad (1)$$

where n denotes the number of magnetic impurity per formula unit, g_J the Lande g -factor, J the angular momentum, μ_B the Bohr magneton, $\alpha \equiv (g_J J \mu_B \mu_0 H)/(k_B T)$, μ_0 the permeability in vacuum and $B_J(\alpha)$ is called Brillouin function,

$$B_J(\alpha) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}\alpha\right) - \frac{1}{2J} \coth\frac{\alpha}{2J}. \quad (2)$$

For a large α (at very low T and/or very high H), M tends to saturate. While for $\alpha \ll 1$ (at high T and/or

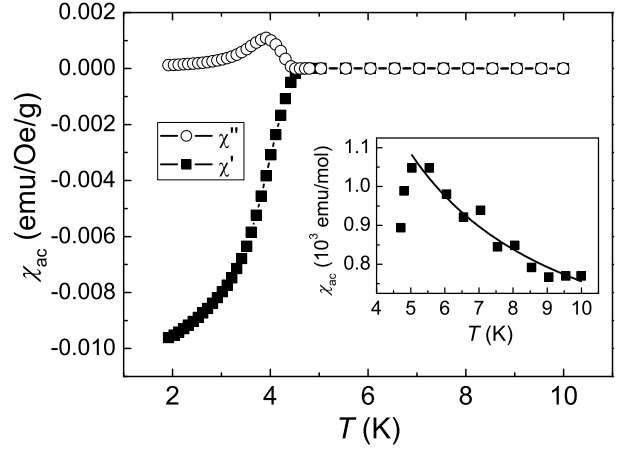


FIG. 1: Temperature dependence of ac magnetic susceptibility for aligned powder sample of $\text{Na}_{0.33}(\text{H}_3\text{O})_{0.02}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ with an ac field of 10 Oe parallel to *ab* planes. χ' and χ'' denote the real and imaginary parts, respectively. The inset is an expanded plot for displaying the normal-state susceptibility. The solid line is a Curie fit with the formula $\chi = \chi_0 + C/T$.

low H), the Brillouin function can be simplified and the susceptibility is given in the form of Curie law,

$$\chi = \frac{M}{H} \approx \frac{n\mu_0\mu_{eff}^2}{3k_B T}, \quad (3)$$

where $\mu_{eff} = g_J \sqrt{J(J+1)}\mu_B$.

For the present study, the total molar magnetization above T_c can be expressed as,

$$M_{tot}(H, T) = \chi_0 H + M(H/T), \quad (4)$$

where χ_0 includes the contribution from Pauli paramagnetism as well as core diamagnetism, which is independent of both temperature and magnetic field. Experimentally, χ_0 value was obtained by the Curie fit shown in the inset of Fig. 1. Therefore, $(M_{tot} - \chi_0 H)$ should be scaled in terms of H/T . As shown in Fig. 2, the T -dependent part of normal-state $M(H, T)$ ($0.1 \text{ T} \leq H \leq 8 \text{ T}$, $5 \text{ K} \leq T \leq 10 \text{ K}$) data actually fall onto the same curve. Furthermore, equation (1) gives a satisfactory fit of the curve. The fitting parameters are $n=0.0014$, $g_J=2.4 \pm 0.1$, $J=1.6 \pm 0.2$. We have also checked validity of the scaling behavior on different samples. The g_J and J value are almost identical for all the samples. However, the n value varies from sample to sample, even for the samples with nearly the same T_c . This sample-dependent behavior strongly suggests that the T -dependence part of the normal-state magnetization is not intrinsic.

As we know, Co^{2+} in the high spin state has $J=S=3/2$ and $g=2.5$, which is very close to the fitting result. Thus, the susceptibility upturn probably arises from the magnetic ion Co^{2+} formed through charge disproportionation

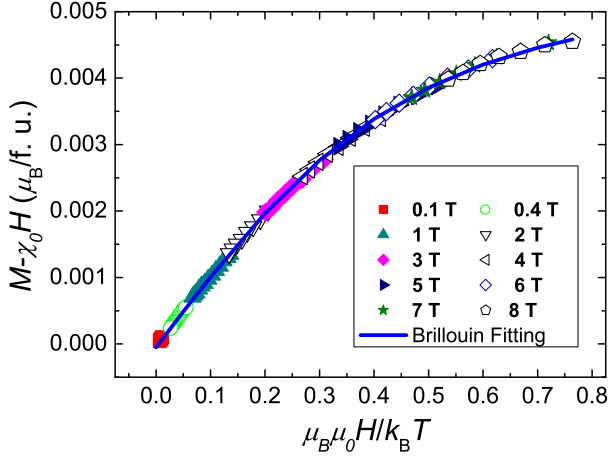


FIG. 2: (Color Online) Scaling behavior of the normal-state magnetization for the aligned $\text{Na}_{0.33}(\text{H}_3\text{O})_{0.02}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ superconductor.

reaction.²³ Since the effective moments of Co^{2+} is $4.8 \mu_B$, according to the Curie fit in the inset of Fig. 1, the Co^{2+} concentration would be 0.13(2) %, consistent with the above Brillouin fitting.

Bearing it in mind that the T -dependent part of normal-state magnetization $M(H, T)$ can be well described by the Brillouin function, we can subtract the magnetic impurity contribution from the total magnetization. After this correction, the superconducting diamagnetism is linear with temperature near the transition region. According to the criterion of the superconducting transition,²⁷ the $T_c(H)$ values were determined as the intersection of linear extrapolation of the magnetization with the base line, as shown in Fig. 3. The result shows that T_c is gradually suppressed with increasing applied field. It is noted that no superconducting transition can be observed under 8 T down to the lowest temperature 1.9 K. This is in sharp contrast with the previous magnetization measurements.⁸ At high fields and low temperatures, in fact, the impurity moments tend to saturate, which could be mistaken for a superconducting transition.

The $H_{c2}^{\parallel ab} - T$ phase diagram obtained is shown in Fig. 4. Our phase diagram is basically in agreement with the measurements from resistivity,¹⁴ thermodynamic^{9,15} and ^{59}Co -NMR.¹⁶ Although the upper critical field at zero temperature $H_{c2}^{\parallel ab}(0)$ could not be directly measured in present work, the rapid decrease of T_c at high magnetic field suggests that $H_{c2}^{\parallel ab}(0)$ is much smaller than those of the previous results by magnetic measurements.^{4,8} In fact, the specific-heat measurement shows no superconducting transition down to 0.6 K at 8 T.¹⁵ That is to say, the $H_{c2}^{\parallel ab}(0)$ value is very close to the Pauli paramagnetic limit $H_P \sim 8.3$ T, supporting spin singlet superconductivity in $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$. It is noted that recent ^{59}Co Knight-shift measurement²⁸ also indicated that the electron pairing in the superconducting state is in the

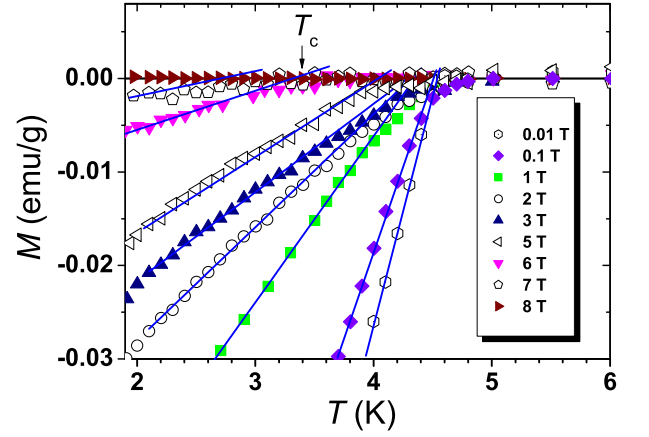


FIG. 3: (Color Online) Temperature dependence of the magnetization (after subtracting the contribution from impurity magnetic moments) under different magnetic field for the aligned $\text{Na}_{0.33}(\text{H}_3\text{O})_{0.02}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ superconductor.

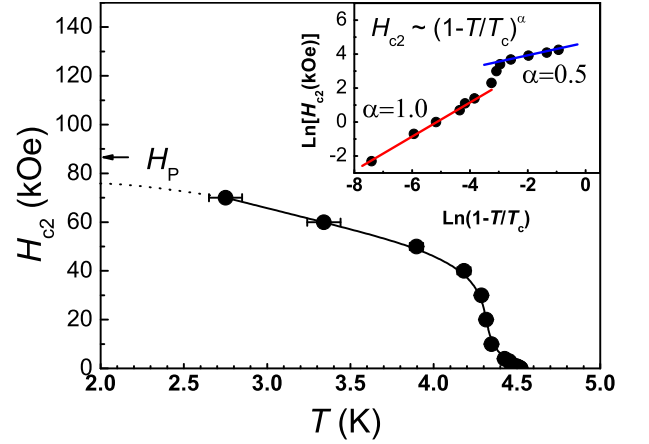


FIG. 4: Temperature dependence of upper critical field $H_{c2}^{\parallel ab}(T)$ for the aligned $\text{Na}_{0.33}(\text{H}_3\text{O})_{0.02}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ superconductor.

spin singlet form.

Fig. 4 also shows that an upward curvature or a slope change near T_c . Since our measurements were performed on aligned samples, the effect of anisotropy of H_{c2} can be ruled out. Therefore, the slope change of $H_{c2}^{\parallel ab}(T)$ should be an intrinsic phenomenon.

There were theoretical explanations for the $H_{c2}(T)$ anomaly in terms of pairing symmetry transition.^{8,19} Considering the two-dimensionality of the present superconductor, here we propose another possibility: a field-induced 3D-to-2D dimensional crossover. As can be seen from the inset of Fig. 4, $H_{c2}^{\parallel ab}(T)$ is proportional to $(1 - T/T_c)$ near T_c , as expected from 3D Ginzburg-Landau theory. On the other hand, $H_{c2}^{\parallel ab}(T)$ is proportional to $(1 - T/T_c)^{1/2}$ for $0.6T_c \leq T \leq 0.95T_c$, which is a signature of decoupled 2D behavior.²⁹ Deutscher *et al.*³⁰ have shown that a layered superconductor built up by

alternating superconducting and insulating layers shows a dimensional crossover characterized by an upturn in $H_{c2}^{\parallel ab}(T)$ at the temperature where interlayer coherence length $\xi_{\perp}(T)$ is of the order of the sum of single superconducting and insulating layers. The $\xi_c(0)$ value of $\sim 13 \text{ \AA}^{14}$ is comparable to the interlayer spacing 9.8 \AA , indicating that the dimensional crossover is probable for the present superconductor. In order to clarify this issue, the measurement of angular dependence of upper critical field on high quality single crystal is highly desired. As is known, in the 3D regime $H_{c2}^{\parallel ab}(\Theta)$ shows a rounded maximum around $\Theta=0$ while in the 2D case it exhibits a cusp.³¹

IV. CONCLUSION

In summary, we have carried out a detailed magnetization measurement on aligned $\text{Na}_{0.33}(\text{H}_3\text{O})_{0.02}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ superconductors with magnetic field parallel to ab planes. The temperature-dependent part of normal-

state magnetization was revealed to arise from paramagnetic impurity rather than spin fluctuations. The onset of superconductivity was characterized by the deviation from normal-state magnetization governed by the Brillouin function. The result suggested that the $H_{c2}^{\parallel ab}(0)$ value for the cobalt oxyhydrate superconductor was just within the Pauli paramagnetic limit $H_P \approx 8.3 \text{ T}$, which supports spin-singlet superconductivity. Besides, the slope change near T_c in $H_{c2}^{\parallel ab} - T$ phase diagram was confirmed to be intrinsic. A field-induced 3D-to-2D dimensional crossover is an alternative explanation for this anomaly, which needs further investigations.

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